CHAPTER IV

ANALYTICAL STUDY
MOLECULAR WEIGHT DETERMINATION BY RAST METHOD
IV Analytical Study

The composition of the structure of the chelates thus prepared has been determined on the basis of:

(1) Molecular Weight Determination by Rast Method.
(2) Job’s Method of Continuous Variation.
(3) Magnetic Susceptibility
(4) And also characterized by decomposition pt.,IR etc (chapter-III)

(IVA) Molecular Weight Determination by Rast’s Method

The molecular weights of the chelates were determined by Rast’s method using pure camphor. The results are recorded in the following table 1 and 2.

In each case

Weight of complex taken = 0.2 gm
Weight of camphor = 2.0 gm
Kf of camphor = 39.68°C / 1000 ml

Table - IVA(1)

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Chelates with 7-hydroxy-8-aceto- N-(4’6’-dichloro 1’,3’,5’-S-triazino) coumarin hydrazone</th>
<th>Depression in F.P.</th>
<th>Molecular Weights</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theoretical (Tc)</td>
<td>Experimental (Tc)</td>
</tr>
<tr>
<td>1.</td>
<td>Cu (C_{14}H_{5}O_{3}N_{2}Cl_{2})</td>
<td>6.69</td>
<td>6.72</td>
</tr>
<tr>
<td>2.</td>
<td>Ni (C_{14}H_{6}O_{2}N_{2}Cl_{2})</td>
<td>6.73</td>
<td>6.71</td>
</tr>
<tr>
<td>3.</td>
<td>Co (C_{14}H_{6}O_{2}N_{2}Cl_{2})</td>
<td>6.73</td>
<td>6.82</td>
</tr>
<tr>
<td>4.</td>
<td>Fe (C_{14}H_{6}O_{2}N_{2}Cl_{2})</td>
<td>12.38</td>
<td>12.27</td>
</tr>
</tbody>
</table>

The results are in agreement with the theoretical composition of the chelates.
Table - IVA(2)

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Chelates with 7-hydroxy-8-aceto coumarin hydrazone</th>
<th>Depression in F.P.</th>
<th>Molecular Weights</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theoretical (T_c)</td>
<td>Experimental (T_o)</td>
</tr>
<tr>
<td>1.</td>
<td>Cu (C_{11}H_{9}O_{3}N_{2})_2</td>
<td>4.19</td>
<td>4.21</td>
</tr>
<tr>
<td>2.</td>
<td>Ni (C_{11}H_{9}O_{3}N_{2})_2</td>
<td>4.21</td>
<td>4.19</td>
</tr>
<tr>
<td>3.</td>
<td>Co (C_{11}H_{9}O_{3}N_{2})_2</td>
<td>4.27</td>
<td>4.27</td>
</tr>
<tr>
<td>4.</td>
<td>Fe (C_{11}H_{9}O_{3}N_{2})_2</td>
<td>8.02</td>
<td>7.9</td>
</tr>
</tbody>
</table>

The results are in agreement with the theoretical composition of the chelates.
CHAPTER IV B

JOB'S METHOD OF CONTINUOUS VARIATION
(IVB) Job’s Method Of Continuous Variation

Job’s method of continuous variation for determining metal: ligand ratio.

In a chemical reaction of the type –

\[ M + n \cdot A = MA_n \]

In which the complex \( MA_n \) is formed from the metal ions “M” and the ligand “A” with same molar concentrations and mixed in varying proportions.

Now, \( M + n \cdot A = MA_n \) \hspace{1cm} \text{(i)}

\[ \therefore \text{Formation constant } K_f = \frac{[MA_n]}{[M] \times [A]^n} \] \hspace{1cm} \text{(ii)}

If we impose the restriction, \([M] + [A] = \text{Const}\), where \([M]\) & \([A]\) denotes conc. of \(M\) & \(A\) respectively.

It can be shown that when concentration of chelate \([MA_n]\) is maximum.

Then, \[ \frac{d[MA_n]}{d[M]} = 0 \] \hspace{1cm} \text{(iii)}

Or, \[ \frac{A}{M} = n \] \hspace{1cm} \text{(iv)}

In other words for a constant total concentration of a metal and the chelating agent in a solution, the concentration of the chelate is the greatest, when the metal and the chelating agents are brought together in the same ratio in which they exist in the chelate. This can be evaluated in terms of optical density. If a solution of a ligand ‘A’ is mixed with solution of metal ion ‘M’ so that the total molar concentration of the ligand plus that of metal ion is maintained constant.

Then, \[ [M] = M_t - [MA_n] \] \hspace{1cm} \text{(v)}

\[ [A] = A_t - [MA_n] \] \hspace{1cm} \text{(vi)}

\[ [M_t] + [A_t] = \text{constant} \] \hspace{1cm} \text{(vii)}

Where \([M_t]\) and \([A_t]\) are the total of ‘M’ and ‘A’taken respectively. The optical density ‘D’ of the solution at a given wavelength represents the total absorbance by all the species in the solution.

\[ D = 1 \cdot (E_1[M] + E_2[A] + E_3[MA_n]) \] \hspace{1cm} \text{(viii)}
Where 'l' is the length of the lightpath through the solution and $E_1$, $E_2$, $E_3$ are respective molar extinction co-efficients of 'M', 'A' and 'MA_n' respectively.

Now, $Y = \{1 \times (E_1[M] + E_2[A] + E_3[MA_n]) - (1 \times E_1[M] + E_2[A])\} \quad \cdots \cdots \text{(ix)}$

Absorbance 'Y' represents the difference in the optical density 'D' shown by equation (VII) and the corresponding optical density that would have resulted if no reaction occurred.

Where the chelating agent (ligand) is transparent to the given wavelength, the equation (IX) may be simplified by assuming $E_2 = 0$, if the cell path (l) is 1 cm the function 'Y' is defined by the relationship.

$$Y = E_1[M] + E_3[An] - E_1[M] \quad \cdots \cdots \text{(x)}$$

Differentiating the equation (X) with respect to $(A_t)$ gives.

$$\frac{dy}{d[A_t]} = E_1 \frac{d[M]}{d[A_t]} - E_1 \frac{d[M]}{d[A_t]} + E_3 \frac{d[MA_n]}{d[A_t]} \quad \cdots \cdots \text{(xi)}$$

Now according to equation (V) $[M] = [M_t] - [MA_n]$

Differentiating with respect to $A_t$

$$\frac{d[M]}{d[A_t]} = \frac{d[M]}{d[A_t]} - \frac{d[MA_n]}{d[A_t]}$$

$$E_1 \frac{d[M]}{d[A_t]} = E_1 \frac{d[M]}{d[A_t]} - E_1 \frac{d[MA_n]}{d[A_t]} \quad \cdots \cdots \text{(xii)}$$

Putting the value of $E_1 \frac{d[M]}{d[A_t]}$ in equation (XI)

$$\frac{dy}{d[A_t]} = E_3 \frac{d[MA_n]}{d[A_t]} - E_1 \frac{d[MA_n]}{d[A_t]}$$

$$\frac{dy}{d[A_t]} = (E_3 - E_1) \frac{d[MA_n]}{d[A_t]} \quad \cdots \cdots \text{(xiii)}$$

Equation (XIII) represents the base for the job's method of continuous variation.

If the chelate is the only coloured substance present, the optical density of the solution is proportional to the concentration of the chelate. Hence the graph of optical density against the volume of the solutions of metal ion as that of the
ligand would give curve with the maximum at the composition corresponding to the formula of the chelate. If the substance present which absorb light in the same region as does chelate, it is necessary to make an allowance for the same. Job[1] observed that this method is not applicable to a system in which more than one compounds are formed.

This method has been used to determine the composition of Cu$^{+2}$, Fe$^{+2}$, Fe$^{+3}$ & Co$^{+2}$ chelates with salicyclic acid derivatives. Foley & Anderson[2], Turner & Anderson[3], Yoe & Harvey[4], Moss & Mellon[5] employed this method for iron & kojic acid. Pandya[6] and Amin[7] used this method to determine the composition of o-hydroxy ketoxime chelates with Cu$^{+2}$, Ni$^{+2}$ & Co$^{+2}$.

**Job's Method**

In the Job method of continuous variation 0.002M ethanolic solutions of all the metal salts were prepared and 0.002M ethanolic solutions of the reagents were used. Same molar concentration of the metal ions and of ligands were used. The solutions of the metal ions and the ligands were mixed in various molar ratios of 1:9, 2:8, 3:7, etc. and buffered maintaining the pH 4.5 for Cu$^{+2}$, pH=5.5 for Ni$^{+2}$, pH=6.5 for Co$^{+2}$, pH=7.5 for Fe$^{+2}$ & pH=7.0 for Fe$^{+3}$. The precipitated complex in each case was extracted by adding 15ml chloroform. The chloroform layer was separated. Water droplets were avoided using centrifuge.

The optical density of the extracted solution of the chelate was noted in each case at wavelengths 440 nm and 570nm. Optical densities at various concentrations (molar ratio of metal ion:ligand) are tabulated and optical density against molar ratio was plotted and the composition of the chelate determined from the graphs (page no. 121 To 130).

The result shows that in case of Cu$^{+2}$, Ni$^{+2}$, Co$^{+2}$ the maximas are obtained when the metal ion : ligand ratio is 1:2.

The above results indicate that the chelates of these ligands with Cu$^{+2}$, Ni$^{+2}$ & Co$^{+2}$ should have the following structure.
In the case of Fe$^{+2}$ & Fe$^{+3}$ the maxima was noted when metal : ligand molar ratio was 1:1.

Feigl and Bondi[8], Cox, Wardlaw and Webster[9] have reported that at a higher pH salicyladoxime gives 1:1 chelate with Cu$^{+2}$. This is probably due to stronger dianionic ligands.

The reagent under investigation formed complexes with Fe$^{+2}$ and Fe$^{+3}$ at higher pH having metal : ligand ratio 1:1. The 1:1 composition is supported by element composition and the result of Job's method of continuous variation[10].
Evaluation Of Stability Constant From Job’s Method

The stability constant was calculated following the conventional relationship for the dissociation reaction:

\[
\text{MLn} \rightleftharpoons \text{M + nL} \\
\text{For g.mole} \quad (1-\alpha) \quad \alpha \quad n\alpha \\
\text{For Cg.mole} \quad c \ (1-\alpha) \quad ac \quad [n \ a \ . \ c]^n
\]

where \( \alpha \) is degree of dissociation of the complex

\[
\text{Stability Constant } K_s = \frac{[ML_n]^{-}}{[M][nL]^n} = \frac{c \ (1-\alpha)}{\alpha \ c \ [n \ a \ . \ c]^n}
\]

Taking \( n=2 \) in this case (for complexes of Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\))

\[
K_s = \frac{1-\alpha}{4 \ \alpha^3 c^2} \quad \text{Where C = concentration g.moles/litre}
\]

Now \( \alpha = \frac{(Em - Es)}{Em} \)

Where \( Em = \) absorbance at formation of MLn (Peak)

and \( Es = \) absorbance at the stoichiometry molar ratio of the metal to reagent in the complex (1:2)

The Stability Constant was calculated determining \( \alpha \) from the graph and putting the value of \( \alpha \) in the above equation stability constant of the chelates of Cu\(^{2+}\), Ni\(^{2+}\), and Co\(^{2+}\) was calculated.

In the case of Fe\(^{2+}\) & Fe\(^{3+}\) Complex. \( n = 1 \) metal ligand ratio is 1:1

\[
\therefore n = 1 \therefore K_s = \frac{[ML_n]}{[M][nL]^n} = \frac{c \ (1-\alpha)}{\alpha \ c \ (n \ a \ . \ c)^n}
\]

Taking \( n=1 \) in this case \( K_s = \frac{(1-\alpha)}{c.\alpha^2} \)

The stability constant was calculated using the above relation, for Fe\(^{2+}\) and Fe\(^{3+}\) chelat

The standard free energy change \( \Delta G^0 \) for the formation reaction of complex has been calculated at 25°C using the formula \( \Delta G^0 = -RT\ln K \)
JOB's Method for
Bis[7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-s-triazino)
coumarin hydrazone] Copper (II)

Reagent :- 0.002 M [7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-s-triazino) coumarin hydrazone] in C_2H_5OH

Metal Solution :- CuCl_2.2H_2O = 0.002 M

Wavelength used
\( \lambda = 440 \text{ nm} \)
\( \lambda = 570 \text{ nm} \)

<table>
<thead>
<tr>
<th>Copper solution Taken ml</th>
<th>Reagent solution ml</th>
<th>Optical Density at ( \lambda = 440 \text{ nm} )</th>
<th>Optical Density at ( \lambda = 570 \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>0.151</td>
<td>0.060</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.316</td>
<td>0.113</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.462</td>
<td>0.171</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.509</td>
<td>0.176</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.426</td>
<td>0.149</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.327</td>
<td>0.120</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.232</td>
<td>0.093</td>
</tr>
</tbody>
</table>

\( \alpha = \frac{E_m - E_s}{E_m} = \frac{0.520 - 0.462}{0.520} = 0.1115 \)

\( K_s = \frac{1 - \alpha}{4 c^2 \alpha^3} = \frac{1 - 0.1115}{4 \times (0.002)^2 \times (0.1115)^3} = 4.02 \times 10^7 \)

\( \Delta G^0 = -RT \ln K = -2.303 \times 1.987 \times 303 \times \log 4.02 \times 10^7 = -10.543 \text{ K.cal/mole} \)
**JOB's Method For**

**Bis[7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-s-triazino)coumarin hydrazone] Nickel (II)**

Reagent: 0.002M [7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-s-triazino)coumarin hydrazone] in C2H5OH

Metal Solution: NiCl2 6H2O = 0.002 M

Wavelength used: \( \lambda = 440 \text{ nm} \)
\( \lambda = 570 \text{ nm} \)

<table>
<thead>
<tr>
<th>Nickel solution Taken</th>
<th>Reagent solution Taken</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml</td>
<td>ml</td>
<td>( \lambda = 440 \text{ nm} )</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>0.051</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.100</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.142</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.145</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.121</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.095</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.070</td>
</tr>
</tbody>
</table>

\( \alpha = \frac{(Em - Es)}{Em} = \frac{0.158 - 0.142}{0.158} = 0.1012 \)

\( Ks = \frac{1 - \alpha}{4 c^2 \alpha^3} = \frac{1 - 0.1012}{4 \times (0.002)^2 \times (0.1012^3)} = 5.453 \times 10^7 \)

\( \Delta G^0 = -RT \ln K = -2.303 \times 1.987 \times 303 \times \log 5.453 \times 10^7 = -10.727 \text{ K.cal/mole} \)
JOB's Method For

Bis[7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-s-triazino)coumarin Hydrazone] Cobalt (II)

Reagent : 0.002M [7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-s-triazino)coumarin hydrazone] in C₂H₅OH

Metal Solution : CoCl₂·6H₂O = 0.002 M

Wavelength used

\( \lambda = 440 \text{ nm} \)

\( \lambda = 570 \text{ nm} \)

<table>
<thead>
<tr>
<th>Cobaltus solution taken ml</th>
<th>Reagent solution ml</th>
<th>Optical Density</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>0.172</td>
<td>0.071</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.359</td>
<td>0.142</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.535</td>
<td>0.203</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.509</td>
<td>0.211</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.410</td>
<td>0.170</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.317</td>
<td>0.132</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.235</td>
<td>0.093</td>
</tr>
</tbody>
</table>

\( \alpha = \frac{Em - Es}{Em} = \frac{0.560 - 0.535}{0.560} = 0.0446 \)

\( K_\text{s} = \frac{1 - \alpha}{4C^2 \alpha^3} = \frac{1 - 0.0446}{4 \times (0.002)^2 \times (0.0446)^3} = 6.73 \times 10^8 \)

\( \Delta G^0 = -RT \ln K = -2.303 \times 1.987 \times 303 \times \log 6.73 \times 10^8 = -12.243 \text{ K.cal/mole} \)

Metal:Ligand ratio 1:2
JOB's Method For
Ferrous(II)[7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-S-triazino)coumarin hydrazone]

Reagent : 0.002M [7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-S-triazino)coumarin hydrazone] in C$_2$H$_5$OH

Metal Solution : FeSO$_4$ (NH$_4$)$_2$ 6H$_2$O = 0.002 M

Wavelength used $\lambda = 0$ 440 nm

$\lambda = \Box$ 570 nm

<table>
<thead>
<tr>
<th>Ferrous solution</th>
<th>Reagent solution</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taken ml</td>
<td>ml</td>
<td>$\lambda=440$ nm</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>0.018</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.031</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.043</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.055</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.067</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.056</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.042</td>
</tr>
</tbody>
</table>

Where $\lambda = 440$ nm

$\alpha = \frac{(Em - Es)}{Em} = \frac{0.070 - 0.067}{0.070} = 0.0428$

$K_s = \frac{1 - \alpha}{c \alpha^2} = \frac{1 - 0.0428}{(0.002) x (0.0428)^2} = 2.658 \times 10^5$

$\Delta G^0 = -RT \ln K = -2.303 \times 1.987 \times 303 \times \log 2.658 \times 10^5 = -7.521 \text{ K}\cdot \text{cal/mole}$
**JOB's Method For**

Ferric(III)[7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-s-triazino)coumarin hydrazone]

Reagent :- 0.002M [7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-s-triazino)coumarin hydrazone] in C₂H₅OH

Metal Solution :- Ferric alum Solution = 0.002 M

Wavelength used  \( \lambda = \text{O} 440 \text{ nm} \)
\( \lambda = \square 570 \text{ nm} \)

<table>
<thead>
<tr>
<th>Ferric solution Taken</th>
<th>Reagent solution Taken</th>
<th>Optical Density</th>
<th>( \lambda = 440 \text{ nm} )</th>
<th>( \lambda = 570 \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml</td>
<td>ml</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>0.009</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.019</td>
<td>0.0085</td>
<td></td>
</tr>
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<td>3</td>
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<td>0.026</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.036</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.042</td>
<td>0.021</td>
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<tr>
<td>6</td>
<td>4</td>
<td>0.034</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.024</td>
<td>0.012</td>
<td></td>
</tr>
</tbody>
</table>

Where  \( \lambda = 440 \text{ nm} \)

\[ \alpha = \frac{(E_m - E_s)}{E_m} = \frac{0.046 - 0.042}{0.046} = 0.0869 \]

\[ K_s = \frac{1 - \alpha}{c \alpha^2} = \frac{1 - 0.0869}{(0.002)^2 x (0.0869)^2} = 6.04 \times 10^4 \]

\[ \Delta G^0 = -RT \ln K = -2.303 \times 2 \times 1.987 \times \log 6.04 \times 10^4 = -6.629 \text{ K.cal/mole} \]
JOB’s Method For
Bis[7-hydroxy-8-aceto coumarin hydrazone] Copper (II)

Reagent :- 0.002 M (7-hydroxy-8-aceto-coumarin hydrazone) in C₂H₅OH
Metal Solution :- CuCl₂ 2H₂O = 0.002 M
Wavelength used \( \lambda = \) O 440 nm
\( \lambda = \) 570 nm

<table>
<thead>
<tr>
<th>Copper Solution Taken ml</th>
<th>Reagent Solution Taken ml</th>
<th>Optical Density ( \lambda=440 ) nm</th>
<th>Optical Density ( \lambda=570 ) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>0.033</td>
<td>0.024</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.061</td>
<td>0.040</td>
</tr>
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<td>3</td>
<td>7</td>
<td>0.089</td>
<td>0.057</td>
</tr>
<tr>
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<td>6</td>
<td>0.086</td>
<td>0.055</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.071</td>
<td>0.046</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.057</td>
<td>0.037</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.045</td>
<td>0.027</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>0.032</td>
<td>0.017</td>
</tr>
</tbody>
</table>

\( \text{Metal:Ligand ratio} 1:2 \)

\[ \alpha = \left( \frac{Em - Es}{Em} \right) = \frac{0.098 - 0.089}{0.098} = 0.0918 \]

\[ K_s = \frac{1 - \alpha}{4 c^2 \alpha^3} = \frac{1 - 0.0918}{4 \times (0.002)^2 \times (0.0918)} = 7.38 \times 10^7 \]

\[ \Delta G^0 = -RT\ln K = -2.303 \times 2 \times 303 \times \log 7.38 \times 10^7 = -10.909 \text{ K.cal/mole} \]
JOB's Method For
Bis[7-hydroxy-8-aceto coumarin hydrazone] Nickel (II)

Reagent: - 0.002 M (7-hydroxy-8-aceto-coumarin hydrazone) in C$_2$H$_5$OH

Metal Solution: - NiCl$_2$ 6H$_2$O = 0.002 M

Wavelength used: $\lambda = \square 440$ nm

$\lambda = \square 570$ nm

<table>
<thead>
<tr>
<th>Nickel solution Taken ml</th>
<th>Reagent solution Taken ml</th>
<th>Optical Density $\lambda$=440 nm</th>
<th>Optical Density $\lambda$=570 nm</th>
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<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>0.039</td>
<td>0.023</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.061</td>
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</tr>
<tr>
<td>3</td>
<td>7</td>
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</tr>
<tr>
<td>4</td>
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<td>0.037</td>
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<tr>
<td>8</td>
<td>2</td>
<td>0.025</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Metal:Ligand ratio 1:2

$$\alpha = \frac{(Em - Es)}{Em} = \frac{0.087 - 0.082}{0.087} = 0.0574$$

$$Ks = \frac{1 - \alpha}{4c^2 \alpha^3} = \frac{1 - 0.0574}{4 \times (0.002)^2 \times (0.0574)^3} = 3.121 \times 10^8$$

$\Delta G^0 = -RT \ln K = -2.303 \times 1.987 \times 303 \times \log 3.121 \times 10^8 = -11.777 \text{ K.cal/mole}$
JOB's Method For
Bis[7-hydroxy-8-aceto coumarin hydrazone] Cobalt (II)

Reagent: - 0.002 M (7-hydroxy-8-aceto-coumarin hydrazone) in C₂H₅OH

Metal Solution: - CoCl₂ 6H₂O = 0.002 M

Wavelength used \( \lambda = 0\,440\,nm \)
\( \lambda = \Box\,570\,nm \)

<table>
<thead>
<tr>
<th>Cobaltus solution Taken ml</th>
<th>Reagent solution ml</th>
<th>Optical Density ( \lambda = 440 ) nm</th>
<th>Optical Density ( \lambda = 570 ) Nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.212</td>
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<tr>
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<td>5</td>
<td>0.290</td>
<td>0.174</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.232</td>
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<td>7</td>
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<td>0.180</td>
<td>0.105</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>0.135</td>
<td>0.072</td>
</tr>
</tbody>
</table>

Where \( \lambda = \text{ligand nm} \)

\[ \alpha = \frac{(Em - Es)}{Em} = \frac{0.400 - 0.366}{0.400} = 0.085 \]

\[ Ks = \frac{1 - \alpha}{4c^2 \alpha^3} = \frac{1 - 0.085}{4 \times (0.002)^2 \times (0.085)^3} = 9.37 \times 10^7 \]

\[ \Delta G^0 = -RT\ln K = -2.303 \times 1.987 \times 303 \times \log 9.37 \times 10^7 = -11.053 \text{ K.cal/mole} \]
JOB's Method For
Ferrous (II) [7-hydroxy-8-aceto coumarin hydrazone]

Reagent: - 0.002 M (7-hydroxy-8-aceto-coumarin hydrazone) in C₂H₅OH
Metal Solution: - FeSO₄ (NH₄)₂ 6H₂O = 0.002 M
Wavelength used  \( \lambda = 440 \text{ nm} \)
\( \lambda = 570 \text{ nm} \)

<table>
<thead>
<tr>
<th>Ferrous solution Taken ml</th>
<th>Reagent solution Taken ml</th>
<th>Optical Density ( \lambda = 440 \text{ nm} )</th>
<th>Optical Density ( \lambda = 570 \text{ nm} )</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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<td>0.050</td>
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<tr>
<td>8</td>
<td>2</td>
<td>0.094</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Metal:Ligand ratio 1:1

\[
\alpha = \frac{(E_m - E_s)}{E_m} = \frac{0.179 - 0.170}{0.179} = 0.0502
\]

\[
K_s = \frac{1 - \alpha}{c \alpha^2} = \frac{1 - 0.0502}{(0.002)(0.0502)^2} = 1.88 \times 10^5
\]

\[
\Delta G^0 = -RT\ln K = -2.303 \times 1.987 \times 303 \times \log 1.88 \times 10^5 = -7.312 \text{ K.cal/mole}
\]
JOB's Method For
Ferric (III) [7-hydroxy-8-aceto coumarin hydrazone]

Reagent :- 0.002 M (7-hydroxy-8-aceto-coumarin hydrazone) in C₂H₅OH
Metal Solution :- Ferric alum Solution = 0.002 M
Wavelength used \( \lambda = 0.440 \text{ nm} \)
\( \lambda = 0.570 \text{ nm} \)

<table>
<thead>
<tr>
<th>Ferric solution Taken ml</th>
<th>Reagent solution ml</th>
<th>Optical Density ( \lambda=440 \text{ nm} )</th>
<th>Optical Density ( \lambda=570 \text{ nm} )</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>0.019</td>
<td>0.016</td>
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<td>2</td>
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</tr>
<tr>
<td>8</td>
<td>2</td>
<td>0.047</td>
<td>0.027</td>
</tr>
</tbody>
</table>

\[ \alpha = \frac{(Em - Es)}{Em} = \frac{0.096 - 0.091}{0.096} = 0.0520 \]

\[ K_s = \frac{1 - \alpha}{c \alpha^2} = \frac{1 - 0.0520}{(0.002)^2 (0.0520)^2} = 1.75 \times 10^5 \]

\[ \Delta G^0 = -RT\ln K = -2.303 \times 1.987 \times 303 \times \log 1.75 \times 10^5 = -7.269 \text{ K.cal/mole} \]

Metal:Ligand ratio 1:1
CHAPTER IV C

MAGNETIC SUSCEPTIBILITY
Magnetic Susceptibility

The use of magnetic properties as a potent tool for the determination of structures of d-transition metal complexes has increased to a considerable extent in the past few years. The study of magnetic property has been found useful in the investigation of the structure of complex compounds. Both the spin and the orbital motion of an electron are sources of magnetic moment. The total magnetic moment of a material is then made up of two components, one due to the electron spin and the other due to the orbital motion of unpaired electrons. In such cases, the spin contribution becomes important, and the orbital contribution being small enough is neglected. Hence the greater portion of the orbital contribution gets cancelled by the interaction of these materials with other ions in solution or in the crystalline state. The most common examples are the ions of the transition group elements. The magnetic moment is given by the following relation.

$$1\text{ B.M.} = \frac{e h}{4\pi m c}$$

Where,
- $h$ = Plank’s Constant = $6.627 \times 10^{-27}$ erg.sec
- $e$ = electronic charge = $4.803 \times 10^{-10}$ esu
- $m$ = mass of electron = $9.109 \times 10^{-28}$ gram
- $c$ = velocity of light = $3 \times 10^{10}$ cm/sec
- B.M. = Bohr magneton = $9.27 \times 10^{-21}$ erg/gauss

Now, the magnetic moment is related to the molar susceptibility ($X_M$) by the Langevin expression:

$$X_M = \frac{N \mu^2 B}{3kT}$$

Where,
- $N$ = Avogadro’s number = $6.02 \times 10^{23}$
- $K$ = Boltzman Constant = $1.38 \times 10^{-16}$
- $T$ = Absolute Temperature
- $B$ = Magnetic Induction
For most cases, permanent moment is given by the expression:

\[ \mu_B = \sqrt{4S(S+1) + L(L+1)} \]

Where,  
\( S \) = the resultant spin angular momentum  
\( L \) = the resultant orbital angular momentum.

For those cases where the orbital contribution is small it can be neglected, the moment then becomes:

\[ \mu_B = \sqrt{4S (S+1)} \]

The number of unpaired electrons \( (n) = 2S \).

Thus the magnetic moment may be related directly to the number of unpaired electrons by the expression:

\[ \mu_B = \sqrt{n(n+2)} \]

The measurement of molar susceptibility \( X_M \), of molecules of transition metal is of a great importance in arriving at conclusion pertaining the number of unpaired electrons and the structure of chelates. Calyin et al.\(^{11}\) corelated the values of \( X_M \) (in emu) with number of unpaired electrons and showed that

\[ X_M \propto n(n+2) \]

Where, \( n \) = number of unpaired electrons.

In the light of this, they established the structures of several bis salicyladimines chelates of Cu\(^{+2}\), Ni\(^{+2}\) and Co\(^{+2}\). This was also supported by X-ray analysis. Mellor and Craig\(^{12}\) pointed out that the chelates of the type given below are covalent or ionic.

\[ \text{N} \quad \text{O} \quad \text{M} \quad \text{N} \quad \text{O} \]

\[ \text{e.g. Co}^{+2} \text{ chelates of above type are reported to be paramagnetic having tetrahedral structure\([13]-[16]\). Ni}^{+2} \text{ chelate of the above type are found to be} \]
diamagnetic. There are no unpaired electron and hence possess square planar structure indicating dsp² hybridization state of the metal[11],[15],[16]. The above generalization was confirmed by X-ray analysis of Nickle-bis-Salicylaldoximes as well as other chelates of Ni⁺²[11],[17],[18],[19].

The study of divalent copper is of great interest since Cu⁺² ion contains one more electron than that in Ni⁺². Although the electronic configuration of Cu⁺² suggests that SP³ hybridization must result. Pauling pointed out that placing the unpaired electron in a 4P orbital requires no loss of energy, and this might result in the stronger dsp² hybridization. Obviously magnetic data would be of little value in this case. However, the X-ray studies indicate[17] that Cu⁺² complexes are not planar. In an arrangement where ‘d’ orbital is not available tetra-hedral complex formation occurs.

Ray & Sen[21] showed that penetration complexes have an unpaired electron in lower lying orbital and hence have a lower magnetic moment and proposed a square planar structure having dsp² hybridization for such chelates. The square planar structure of Cu⁺² chelates of the above type is also supported, by the study of cotton effect[22]. Kato, Jonassen and Fanning[23] reviewed Cu⁺² complexes with subnormal magnetic moments and attributed this to a dimeric structure with Cu-Cu linkage which gives an absorption band at 375 nm[24], [25].

Molar susceptibility $X_M$ can be measured by Gouy’s method. This method involves the use of cylindrical specimen of the material in a region of nonuniform field. The force acting on the rod in air after necessary correction is given by the expression:

$$F = \frac{1}{2} A(K_1-K_2) (H^2 - H_0^2) + \delta$$

Where, 
- $A$ = Cross-section area of the specimen
- $H$ = Magnetic field
- $H_0$ = Field in the region out of the influence of magnet
- $K_1$ = Volume susceptibility of the specimen
- $K_2$ = Volume susceptibility of air
- $\delta$ = Tube correction (constant of the tube)
In practice $H_0$ is the level where magnetic field is very small or zero is marked on the Guoy tube. Therefore $A(H^2 - H_0^2)$ is constant for a given set and hence can be expressed as:

$$X = \frac{(BF' + x)}{W} \quad (F' = F + P)$$

Where,

- $\alpha = K \times$ specimen Volume
- $K = \text{Vol. susceptibility of air per ml} = 0.029 \times 10^{-6}$
  \hspace{1cm} = 0.029 \times 10^{-6} \times$ specimen volume
- $\beta = \text{Tube calibration constant for definite value of H}$
- $H = \text{applied mag. field}$
- $W = \text{Weight of substance taken in Guoy tube}$
- $F = \text{Change in weight of substance on application of magnetic field.}$
- $P = \text{Change in weight of empty tube on application of magnetic field. (due to diamagnetic air in it)}$

The magnetic susceptibility of the chelates was measured using the above relation at a constant temperature.

Magnetic balance is frequently calibrated with the air of substance of known susceptibility. The Gouy balance is often calibrated with water. Two very good solid calibrants are HgCo(CNS)$_4$ and Ni(en)$_3$S$_2$O$_3$. They do not decompose or absorb moisture and packs well. Their susceptibilities at 20°C are 16.44×10$^{-6}$ and 11.03×10$^{-6}$ CGS unit decreasing by 0.05×10$^{-6}$ and 0.04×10$^{-6}$ per degree temperature rise respectively. The Cobalt Compound is suitable for calibrating at low field. While Ni compound suitable for calibrating at high fields. Water being a liquid calibrant eliminate any possible packing error and is to be preferred. The susceptibility of pure water is $-0.720 \times 10^{-6}$ CGS unit and increases approximately $0.0009 \times 10^{-6}$ per degree rise in temperature nearly to upto 20°C.

The calibration of the Gouy balance has been investigated by Angus[26, 27] who pointed out that the water, as a calibrating agent, had some deficiencies and therefore he recommended benzene as calibrating agent. However, it has
been pointed out that oxygen is fairly soluble in benzene. A carefully prepared solution of nickel chloride is useful as a calibrating agent. This solution has been investigated by Brant, Carbera, Moles & Guzman, Weiss & Bruins and by Nettleton and Sugden.

In the present work, distilled-water, which is free from dissolved air, was used for calibration.

In the broad outline of the crystal field theory, the energy levels of ‘d’ orbitals of transition metal ions undergo splitting in an octahedral or tetrahedral field. The octahedral splitting undergoes further deviation leading to a square planar structure according to Jahn-Teller theorem which says that if a non-linear molecule has a degenerate state, then there is at least one vibrational coordinate along which a distortion can occur so as to remove the degeneracy.
Magnetic Susceptibility Measurement Using Gouy’s Balance

The chelate of 7-hydroxy-8-aceto coumarin hydrazone & 7-hydroxy-8-aceto - N-(4’,6’-dichloro-1’,3’,5’-S-triazino)coumarin hydrazone with Cu²⁺, Ni²⁺, Co²⁺, Fe²⁺ & Fe³⁺ were crystallized from ethanol and dried at 100-110°C. Standard “selecta Sartorius” single pan, semi-micro balance was used. This is air-damped and has a sensitivity of 0.01 mg. Schematic diagram of selecta sartorius balance is given at page No.-143.

The Gouy tube was thoroughly cleaned with chromic acid, washed and rinsed several times with distilled water and then with acetone. The tube was then dried in an air-oven maintained at about 100°-110°C.

The specimen tube, used in this work, was made from hard pyrex glass tubing about 1 mm in thickness and having a uniform bore of about 0.5 cm. The length of the tube was about 10cms and it was provided with a ground glass stopper. A mark was etched on the outside of the tube at about 7.5cms, from the bottom. All the substances measured were packed or filled up to this mark.

The tube was vertically suspended by means of a suitable glass collar whose horizontal arms rested on the y-shaped phosphor bronze suspension in such a way that the lower end of the tube hung symmetrically in the center of the electromagnets pole gap.

The Gouy tube was filled with the compound by constant taping the tube to filled up to the upper mark, (where H₀ is nearly zero)

The specimen tube was suspended carefully on the hook between poles of a magnet so that each end was maintained in the region of uniform field. In order to fix the height of the specimen column at which the field is nearly zero, the specimen tube was filled with distilled water free from dissolved air to different heights and the magnitudes of the force in the magnetic field were measured at these heights. The height beyond which there was no change in the magnitude of the force acting on the distilled water free from dissolved air was fixed at the height of the specimen column. A circular mark was etched to indicate
the height. The empty tube was then accurately weighed in presence of and in absence of magnetic field.

This procedure was repeated twice using the empty tube (filled with air) and the mean value of such reading was obtained. The difference between the two weights: (i) in presence of the magnetic field & (ii) in absence of magnetic field, gave a measure of the force the air in the tube in the presence of the magnetic field. The tube was then removed from the suspension and filled with specimen under investigation upto the mark. The tube was then re-suspended and the electro-magnetic box was closed. The readings were taken in the same manner as for the empty tube. Five such readings were taken. The tube was then cleaned and dried. Measurements on the same specimen were made with different packing.

In this investigation values of magnetic susceptibilities have been determined with the help of a standard substance. The choice of the standard substance was made after carefully examining the substance used by different workers for calibration. The standard substance used was distilled water free from dissolved air.

It has been shown earlier that the susceptibility per unit mass \( X \) is given by:

\[
X = \frac{(\beta F' + \alpha)}{w}, \quad \text{where } \alpha = K.V. \text{ (Angus and Tilsten}^{33})
\]

\[
X = \frac{(KV + \beta F')}{W}
\]

where, \( K \) = Volume susceptibility of air per unit volume = \( 0.029 \times 10^{-6} \) emu

\( V \) = Volume of water (or air)

\( \beta \) = Tube calibration constant

\( W \) = Weight of substance

\( F' \) = Apparent change in weight

i.e. force exerted on the specimen by the magnetic field
\[ \propto = K \times V = \text{volume susceptibility per unit volume of air} \times \text{In specimen tube volume of air} \text{ (Angus and Tilsten)} \]

The data on the magnetic moment indicate distorted octahedral, square planar, low spin tetrahedral and octahedral geometry for the copper (II), Nickel (II), Cobalt (II), Iron (II) and Iron (III) complexes respectively.

Magnetic susceptibility of the compounds is determined using the equation:

\[ X = \frac{(KV + 6F)}{W} \]

- \( X \) = Magnetic susceptibility of the compound
- \( K \) = Volume susceptibility of air = 0.029 \times 10^{-6} \text{ per unit volume}
- \( V \) = Volume of air (In Specimen tube)
- \( B \) = Calibration constant, at definite magnetic field \((H)\)
- \( F \) = Change in weight of the compound due to applied magnetic field.

(i) Determination of \( \beta \) using water (free from air) as calibrant magnetic field produced by passing at 4 ampere current

Apparent decrease in weight of air(in specimen tube)

\[ = \text{Difference in wt. of Guoy tube in presence and absence of magnetic field} \]
\[ = (11.6757 - 11.6772)\text{g} \]
\[ = - 0.0015 \text{g} \quad \ldots \ldots \ldots \ldots (i) \]

Apparent decrease in weight of water taken as calibrant(in the tube)

\[ = \text{Difference in wt of (Guoy tube + water) in presence and absence of magnetic field.} \]
\[ = (12.178 - 12.1816)\text{g} \]
\[ W(\text{water}) = - 0.0028 \text{g} \quad \ldots \ldots \ldots \ldots (ii) \]

Change in weight of the calibrant water with diamagnetic correction (i) + (ii)

\[ = (-0.028) + (-0.0015) = -0.0043 \text{ g} \]

Weight of the calibrant water = wt. of (Gouy tube + water) − wt. of Gouy tube

Weight of the calibrant water = \((12.1816 - 11.6772)\text{g}\)
\[ W = 0.5044 \text{ g} \approx 0.5044 \text{ ml} \]

Magnetic susceptibility of water \( X(\text{water}) \) (calibrant) = \(-0.72 \times 10^{-6} \text{ emu}\)

Now \( \beta = \frac{(X_{\text{calibrant}} \times W_{\text{water}} - K_{\text{per ml}} \times V_{\text{air}})}{\text{change in wt of water due to magnetic field with diamagnetic correction}} \)

\[ = \frac{(-0.72 \times 10^{-6} \times 0.5044) - (0.029 \times 10^{-6} \times 0.5044)}{-0.0043} \]

\[ = 87.86 \times 10^{-6} \text{ emu} \] (constant at const. temperature same specimen tube and constant applied magnetic field.)

where,
\( K = \text{vol susceptibility air per unit volume}, V = \text{volume of water(of air) in tube} \)

(ii) **Determination of magnetic susceptibility of Bis[7-hydroxy-8-aceto-N-(4',6'-dichloro-1',3',5'-S-triazino)coumarin HydrazonelCopper(II)**

Weight of the chelate = \( W(\text{chelate}) = \text{wt. of (Gouy tube + complex) - (wt. of Gouy tube)} \)

\[ = (12.4470 - 11.6772)\text{g} \]
\[ = 0.7698\text{g} \]

Change in weight of the chelate = Difference in wt. of (Gouy tube + Chelate) in presence and absence of magnetic field.

\[ F = (12.590 - 12.447)\text{g} \]
\[ = 0.0143\text{g} \]

Magnetic Susceptibility of the chelate per gram

\[ X = \frac{(KV + \beta F)}{W(\text{chelate})} \]

\[ X = \frac{(-0.029 \times 10^{-6} \times 0.5044 + 87.86 \times 10^{-6} \times 0.0143)}{0.7698} \]

\[ \therefore X = 1.65 \times 10^{-6} \text{ emu per unit mass} \]
Molar Magnetic Susceptibility = \( X_m = X \times \text{molecular weight of the chelate} \)
\[ = 1.65 \times 10^{-6} \times 793.5 = 1309.27 \times 10^{-6} \text{ emu} \]

Magnetic moment of the Cu(II) chelate \( \mu_{\text{eff}} = 2.83 \sqrt{X_m \times T} \) B.M.
(\( \text{where} \ T = 303^\circ \text{K} \))
\[ \mu_{\text{eff}} = 2.83 \sqrt{[1309.27 \times 10^{-6}] \times 303} \]
\[ = 1.77 \text{ B. M.} \]

\[ \mu_{\text{eff}} = \sqrt{n(n+2)} \text{ where, } n = \text{unpaired no. of electronics} \]
\[ 1.77 = \sqrt{n(n+2)} \quad n = 1 \]

Actual volume \( \approx 1 \)

Electronic configuration of \( \text{Cu}_{29} = [\text{Ar}] 4s^1 3d^{10} \) & \( \text{Cu}^{2+} = [\text{Ar}] 4s^0 3d^9 \)

eg ligands therefore Cu(II) chelates probably has Td structure.

---

Field with electron of ligand

**Giving SP\(^3\) hybridization**
Table – IVC(1)

Chelate with 7-hydroxy-8-aceto-N-(4'6'-dichloro 1'3'5'-S-triazino) cou

<table>
<thead>
<tr>
<th>Comp. Name</th>
<th>Wt. of the comp. = W= (wt. of tube + comp) – wt. of empty tube</th>
<th>Change in wt. in mag. Field = F</th>
<th>Mag. Sus. Per unit mass X= (KV+\beta F)/W</th>
<th>Molar Mag. Sus. Xm = \chi \times \text{mol wt. (emu)}</th>
<th>Mag. Moment in hydrazone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)comp.</td>
<td>(12.4462 -11.6772) =0.769g</td>
<td>(12.590 -12.12447) =0.0143g</td>
<td>(- 0.029\times 10^5 + 0.5044 + 87.86\times 10^6 \times 0.0143)/0.769 =1.65\times 10^6 \times 793.5 =1309.27\times 10^6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(II)comp.</td>
<td>(12.2572 -11.6772) =0.580g</td>
<td>Wt. was found to decrease</td>
<td></td>
<td></td>
<td>83 \sqrt{1309.27 \times \text{M}} =1.77 \text{B.M}</td>
</tr>
<tr>
<td>Co(II)comp.</td>
<td>(12.3282 -11.6772) =0.651g</td>
<td>(12.3397 -12.3282) =0.0115g</td>
<td>(- 0.029\times 10^5 + 0.5044 + 87.86\times 10^6 \times 0.0115)/0.651 =1.57\times 10^6 \times 789.93 =1238\times 10^6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(II)comp.</td>
<td>(12.2772 -11.6772) =0.600g</td>
<td>(12.3702 -12.2772) =0.093g</td>
<td>(- 0.029\times 10^5 + 0.5044 + 87.86\times 10^6 \times 0.093)/0.6 =13.64\times 10^6 \times 785.84 =10710\times 10^6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(III)comp.</td>
<td>(12.2672 -11.6772) =0.59g</td>
<td>(12.3909 -12.2672) =0.1237g</td>
<td>(- 0.029\times 10^5 + 0.5044 + 87.86\times 10^6 \times 0.1237)/0.59 =18.56\times 10^6 \times 785.84 =14580\times 10^6</td>
<td></td>
<td>83 \sqrt{14580 \times 10^6 \times 303} =5.93 \text{B.M}</td>
</tr>
</tbody>
</table>

N.B. The calibrant constant \( \beta = 87.86 \times 10^{-6} \text{emu} \) determined for same tube and same field. \( K = \text{magnetic susceptibility of air of} \beta = 87.86 \times 10^{-6} \text{emu} \) for unit volume, \( T = \text{Cu}^{2+} \text{is [Ar] 4s}^0 \text{3d}^9 \) Hence probable structure of Cu-chelate is (Td) tetrahedral. Si planar and probable structure of Cobalt-chelate is square planar.

\[
\begin{align*}
\mu_{\text{eff}} &= 2.83 \sqrt{X_m T} \\
\text{Mag. Moment} &= \sqrt{n(n+2)} \\
\text{Property} &= 83 \sqrt{1309.27} \times 303 = 1.77 \text{B.M} \\
\text{n = 1} &\quad \text{Paramagnetic} \\
\text{n = 0} &\quad \text{Diamagnetic} \\
\text{n = 4} &\quad \text{Paramagnetic} \\
\text{n = 5} &\quad \text{Paramagnetic}
\end{align*}
\]
All compounds were filled (using the same Gouy tube) up to the upper mark of the Gouy tube. The temperature 30\(\pm\) 273°K. The magnetic field applied kept constant was \(B = 87.86 \times 10^{-6}\) (determined) used in all cases.

Table – IV-C(2)

<table>
<thead>
<tr>
<th>Name of compound</th>
<th>wt. of the comp.=W = wt. of (tube + comp.) – wt. of empty tube</th>
<th>Change in wt. in mag. field = F</th>
<th>Mag. Susc. Per unit mass of comp. (X = (KV + BF)/W)</th>
<th>Molar Mag.Susc. (Xm = 2^a\text{mol.wt.})</th>
<th>Mag. Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)comp.</td>
<td>(12.2382 - 11.6772) = 0.561g</td>
<td>(12.2522 - 12.2382) = 0.014g</td>
<td>((-0.029 \times 10^6 \times 0.5044 + 87.86 \times 10^{-6} \times 0.014) + 0.561 \times 2.218 \times 10^6 \text{emu})</td>
<td>((2.218 \times 10^6 \times 497.54) = 103 \times 10^{-6} \text{emu})</td>
<td>(\mu_{eff} = \sqrt{n(n+2)}\text{, no. of unpaired ele. } n = 3\text{, } n \approx 1\text{, Paramagnetic})</td>
</tr>
<tr>
<td>Ni(II)comp.</td>
<td>(12.2082 - 11.6772) = 0.531g</td>
<td>Wt. decreases</td>
<td>(-0.029 \times 10^6 \times 0.5044 + 87.86 \times 10^{-6} \times 0.01562 + 0.542 \times 2.56 \times 10^6 \text{emu})</td>
<td>((2.56 \times 10^6 \times 492.93) = 1262 \times 10^{-6} \text{emu})</td>
<td>(n = 1\text{, } n \approx 1\text{, Paramagnetic})</td>
</tr>
<tr>
<td>Co(II)comp.</td>
<td>(12.2192 - 11.6772) = 0.542g</td>
<td>(12.23483 - 12.2192) = 0.01563g</td>
<td>((-0.029 \times 10^6 \times 0.5044 + 87.86 \times 10^{-6} \times 0.01562 + 0.542 \times 2.56 \times 10^6 \text{emu})</td>
<td>((2.56 \times 10^6 \times 492.93) = 1262 \times 10^{-6} \text{emu})</td>
<td>(n = 1\text{, } n \approx 1\text{, Paramagnetic})</td>
</tr>
<tr>
<td>Fe(II)comp.</td>
<td>(12.1992 - 11.6772) = 0.522g</td>
<td>(12.3129 - 12.1992) = 0.1137g</td>
<td>((-0.029 \times 10^6 \times 0.5044 + 87.86 \times 10^{-6} \times 0.01137 + 0.522 \times 21.82 \times 10^6 \text{emu})</td>
<td>((21.82 \times 10^6 \times 489.84) = 10675 \times 10^{-6} \text{emu})</td>
<td>(n = 4\text{, } n \approx 4\text{, Paramagnetic})</td>
</tr>
<tr>
<td>Fe(II)comp.</td>
<td>(12.1942- 11.6772=0.517g</td>
<td>(12.3722 - 12.1942=0.178g)</td>
<td>((-0.029 \times 10^6 \times 0.5044 + 87.86 \times 10^{-6} \times 0.178 + 0.517 \times 30.33 \times 10^6 \text{emu})</td>
<td>((30.33 \times 10^6 \times 489.84) = 14889 \times 10^{-6} \text{emu})</td>
<td>(n = 5\text{, } n \approx 5\text{, Paramagnetic})</td>
</tr>
</tbody>
</table>

Electronic configuration of Cu\(^{+}\) is [Ar] 4s\(^{1}\) 3d\(^{9}\) Hence probable structure of Cu-chelate is (Td) tetr square planar and probable structure of Cobalt-chelate is square planar.
Schematic diagram of "Selecta Sartorius" balance.
References

   71, 909, (1949)
8. Feigl F and Bondi A,; *Ber. 64*, 2819, (1931)
20. Pauling D,; "*The nature of the chemical bonding*", 2nd Ed. Ch.II C.U. Press, Ithaca (1940)
29. Brant L.; Phys, Rev, 17, 678, (1921)
30. Cabrera B., Moles E and Guzman J.; Arch. sci. phys.nat, 37, 324, (1914)